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## **Nickel and cobalt complexes of 15,15-disubstituted 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione ligands**

Da Pieve, Chiara ; Spingler, Bernhard

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DOI: <https://doi.org/10.1016/j.ica.2011.09.004>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-65335>

Journal Article

Accepted Version

Originally published at:

Da Pieve, Chiara; Spingler, Bernhard (2012). Nickel and cobalt complexes of 15,15-disubstituted 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione ligands. *Inorganica Chimica Acta*, 380:230-235.

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# **Nickel and cobalt complexes of 15,15-disubstituted 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione ligands**

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## **Abstract**

The synthesis of the novel Co(III)(15,15-difluoro-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione) acetate complex from different cobalt sources is described. Furthermore, the corresponding nickel complex and its new analog with the 15-fluoro-15-methyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione ligand were studied in great detail including cyclic voltammetry and single crystal analysis of a total of 6 complexes. The results for the nickel compounds showed that depending upon ligand substitution and solvent, an N3 or, after a double deprotonation, an N5 coordination mode could be observed and characterized in the solid state and in solution. Moreover, cyclic voltammetric analyses were performed revealing that the Ni(II/III) oxidation potentials are becoming more positive with the increasing number of fluorine atoms. This effect is due to the electron withdrawing property of fluorine that is reducing the electron richness of the metal ion.

*Keywords:* Nickel (II) complexes, Cobalt(III) complexes, azamacrocycles, 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, X-ray crystal structure analysis.

## 1. Introduction

Azamacrocycles are popular ligands for the preparation of metal complexes because of their stability, defined geometry and yet they often possess enough conformational freedom for their intended functionality [1,2]. The macrocycle 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione (**H<sub>2</sub>dione**, **1**) can bind to the metal centre by either triple coordination (N3) or by employing all its five nitrogen atoms (N5) [3-5]. The N5 coordination is preceded by a deprotonation of both amides and is thus favoured by electron withdrawing substituents at the C(15) position (Fig.1).

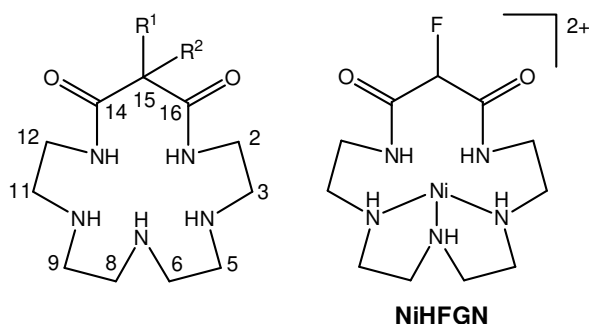


Fig. 1. Structures of the ligands (left) and **NiHFGN** (right). Left: **H<sub>2</sub>dione** (**1**,  $R^1 = R^2 = H$ ), **H<sub>2</sub>FMedione** (**2**,  $R^1 = F$ ,  $R^2 = Me$ ), and **H<sub>2</sub>F<sub>2</sub>dione** (**3**,  $R^1 = R^2 = F$ ).

Kimura and co-worker studied nickel dione complexes and their inhibition of the enzyme superoxide dismutase [6]. Additionally, some derivatives of these complexes have been shown to interact with and activate dioxygen [7-9]. The question whether the Ni-dione complex in its neutral or dicationic form is able to generate methane from the cofactor methyl coenzyme-M, has been contradictorily discussed in the literature [10,11]. Rokita and co-workers synthesised the small azamacrocyclic Ni(II) complex (**NiHFGN**, Fig. 1) and showed that it binds to N7 of guanine and promotes

the conversion of poly d(GC) from B to Z form in a molar ratio complex:nucleotides = 1:3 [12,13].

We have previously studied and reported the influence of methyl versus fluorine substitution at the position 15 of **dione** for zinc and copper complexes [5,14,15] as well as the induction of Z-DNA by mono- and dinuclear complexes [16,17]. We have also optimized the synthesis of non-fluorine substituted **dione** ligands [18]. In this work, we describe the synthesis of **H<sub>2</sub>FMedione (2)** and **H<sub>2</sub>F<sub>2</sub>dione (3)** complexes with nickel(II), their crystal structures and cyclic voltammetric characteristics. Moreover, since cobalt(II) complexes are known to react with oxygen in order to yield very diverse oxygen-cobalt(III) adducts [19-24], we also studied the reaction of Co(II) with **H<sub>2</sub>F<sub>2</sub>dione (3)** and the subsequent oxidation by air.

## 2. Experimental

### 2.1. General

Chemicals were purchased from Aldrich or Fluka and used without further purification. The ligands **2\*1.5HCl** and **3** were synthesised according to the literature [5,25]. Elemental analyses were performed on a Leco CHNS-932 elemental analyser. UV/Vis spectra were recorded on a Varian Cary 50 spectrometer. IR spectra were recorded on a Perkin Elmer BX FT-IR spectrometer using samples in KBr pellets. Fast Atom Bombardment (FAB) mass spectra were recorded on a Finnigan MAT Mass Spectrometer model 8230 equipped with an ION Tech ionisator (Teddington England). The samples were dissolved in ethylene glycol and *para*-nitrobenzyl alcohol (*p*NBA) was used as matrix. ESI-MS were performed on a Merck-Hitachi M-

8000 spectrometer.  $^1\text{H}$ -NMR spectra were recorded on a Varian Gemini 300 MHz. The chemical shifts are relative to residual solvent protons as reference.

## 2.2. *Crystal structure determinations*

Crystallographic data were collected on a Stoe IPDS diffractometer at 183(2) K using a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Suitable crystals were covered with Paratone N oil, mounted on top of a glass fibre and immediately transferred to the diffractometer. Eight thousand reflections distributed over the whole limiting sphere were selected by the program SELECT and used for unit cell parameter refinement with the program CELL [26]. Data were collected for Lorentz and polarisation effects as well as for absorption (numerical). Structures were solved with direct methods using SIR97 [27] and were refined by full-matrix least-squares methods on  $F^2$  with SHELXL-97 [28]. CCDC 290875, 290876 and 834703 - 834706 contain the supplementary crystallographic data for this paper (Table 1). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/ data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1: Crystallographic data

	<b>[Co(F<sub>2</sub>dione)(OAc)] *H<sub>2</sub>O (5)</b>	<b>[Ni(H<sub>2</sub>F<sub>2</sub>dione) (OAc)<sub>2</sub>] (6)</b>	<b>[Ni(F<sub>2</sub>dione)(MeOH)] *MeOH (7)</b>	<b>[Ni(FMedione)Cl<sub>2</sub>] (8)</b>	<b>[Ni(H<sub>2</sub>FMedione)(OAc)<sub>2</sub>]<sub>2</sub> *MeOH (9)</b>
Empirical formula	C <sub>13</sub> H <sub>24</sub> CoF <sub>2</sub> N <sub>5</sub> O <sub>5</sub>	C <sub>15</sub> H <sub>27</sub> F <sub>2</sub> N <sub>5</sub> NiO <sub>6</sub>	C <sub>13</sub> H <sub>27</sub> F <sub>2</sub> N <sub>5</sub> NiO <sub>4</sub>	C <sub>12</sub> H <sub>24</sub> Cl <sub>2</sub> FN <sub>5</sub> NiO <sub>2</sub>	C <sub>33</sub> H <sub>64</sub> F <sub>2</sub> N <sub>10</sub> Ni <sub>2</sub> O <sub>13</sub>
Colour	purple	light blue	pink	green	light blue
Formula weight [g mol <sup>-1</sup> ]	427.30	470.13	414.11	418.97	964.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Crystal dimensions (mm)	0.39x0.37x0.15	0.67 x 0.47 x 0.27	0.4 x 0.1 x 0.1	0.16 x 0.11 x 0.03	0.19 x 0.18 x 0.12
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub>	P2 <sub>1</sub> /c	P-1	P-1
a [Å]	8.8517(7)	15.9860(10)	9.3449(7)	8.9399(9)	10.2880(6)
b [Å]	13.9761(8)	12.7589(5)	12.8849(8)	10.0561(13)	12.8769(8)
c [Å]	13.1597(10)	20.4442(12)	14.9659(11)	10.1533(12)	18.6156(12)
α [°]	90	90	90	84.798(14)	109.458(7)
β [°]	90.369(9)	101.752(7)	90.161(9)	82.275(13)	104.303(7)
γ [°]	90	90	90	87.922(14)	92.159(7)

Volume [ $\text{\AA}^3$ ]	1628.0(2)	4082.5(4)	1802.0(2)	827.88(14)	2233.7(2)
Z	4	8	4	2	2
Absorp. Coeff. ( $\mu$ , $\text{mm}^{-1}$ )	1.115	1.010	1.125	1.398	0.921
Theta range of data [ $^\circ$ ]	2.72 to 30.48	2.70 to 30.43	2.69 to 30.50	2.75 to 30.51	3.17 to 30.45
Reflections collected	30930	88836	16980	12685	30046
Independent reflections	4936 [R(int) = 0.0603]	= 24560 [R(int) = 0.1040]	5394 [R(int) = 0.0935]	4983 [R(int) = 0.0872]	12347 [R(int) = 0.0521]
Data/restraints/parameters	4936/0/245	24560/1/1132	5394/0/243	4983/5/228	12347/0/592
Goodness-on-fit on $F^2$	1.084	0.930	0.818	1.043	1.037
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0479 wR2 = 0.1349	R1 = 0.0458 wR2 = 0.1128	R1 = 0.0600 wR2 = 0.1423	R1 = 0.0545 wR2 = 0.1387	R1 = 0.0574 wR2 = 0.1556
Flack parameter		0.014(7)			
Largest diff. peaks ( $e \text{\AA}^{-3}$ )	0.647 and $-1.202$	0.653 and $-0.404$	0.872 and $-0.528$	0.546 and $-0.418$	0.880 and $-0.783$



*2.3. Reaction of 15,15-difluoro-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione ( $H_2F_2$ dione, **3**) with either  $Co(acac)_3$  or  $Co(II)$  acetate*

Method A: The ligand **3** (50 mg, 0.17 mmol) and  $Co(acac)_3$  (72.9 mg, 0.20 mmol) were suspended in  $CH_3CN$  and refluxed under  $N_2$  for 3 days. The solvent was removed and the pink residue was suspended with  $CH_2Cl_2$ . The mixture was filtrated and a pink precipitate **4** (20.4 mg, 27%) was isolated. Crystals suitable for X-ray crystallography were grown by vapour diffusion of tetrahydropyran into a solution of methanol and aqueous ammonium acetate.

Method B: A solution of **3** (50 mg, 0.17 mmol) in 3 ml of absolute ethanol was added drop-wise to a solution of 42.5 mg of cobalt (II) acetate  $\cdot 4H_2O$  (0.17 mmol) in 10 ml of absolute ethanol. Air was bubbled through the solution for 2 h. The mixture was filtrated and the ethanol was removed under vacuum to give a purple residue **5**. Yield 68.4 mg (98%). Crystals suitable for X-ray crystallography were grown by slow evaporation of a water/methanol mixture. MS (FAB, solvent = ethylene glycol; matrix = *p*NBA):  $m/z$  (%) = 350 (100)  $[M]^+$ , 410 (65.4)  $[M + acetate + H]^+$ .  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 1.72 (s, 3H,  $MeCOO^-$ ), 2.11-2.21 (m, 2H), 2.68-2.97 (m, 8H), 3.23-3.81 (m, 6H). Anal. calc. for  $C_{13}H_{22}CoF_2N_5O_4 \cdot H_2O$ : C, 36.54; H, 5.66; N, 16.39; found: C, 36.68; H, 5.77; N, 16.01. IR (KBr):  $1631\text{ cm}^{-1}$   $\nu$   $C=O_{\text{ligand}}$ ,  $1544\text{ cm}^{-1}$   $\nu$   $C=O_{\text{acetate}}$ . UV-Vis ( $10^{-3}$  M, 1 mM Na-cacodylate buffer, pH = 7):  $\lambda_{\text{max}}$  = 529 nm ( $\epsilon$  =  $185\text{ cm}^{-1}\text{M}^{-1}$ ).

*2.4 Synthesis of the Ni (II) complexes of **3***

The ligand **3** (50 mg, 0.17 mmol) was added to a solution of 42.4 mg of nickel acetate \* 4H<sub>2</sub>O (0.17 mmol) in 10 ml of dry ethanol. The solution was refluxed for 3 h. The mixture was filtrated and then the solvent was removed under vacuum to obtain a light blue product **6** in quantitative yield. Pink crystals **7** were obtained by layering diethyl ether over a methanol solution of the complex.

Analysis of **6**:

**MS (ESI)**: m/z (%) = 349 (100) [M - 2acetate]<sup>+</sup>.

**EA** calcd for C<sub>15</sub>H<sub>27</sub>F<sub>2</sub>N<sub>5</sub>NiO<sub>6</sub>: C, 38.32; H, 5.78; N, 14.89; found: C, 38.12; H, 5.39; N, 15.06.

**IR** (KBr): 1720 cm<sup>-1</sup> ν C=O<sub>ligand</sub>, 1570 cm<sup>-1</sup> ν C=O<sub>acetate</sub>

**UV-Vis** (10<sup>-2</sup> M) 1 mM Na- cacodylate buffer, pH = 7: λ<sub>max</sub> = 528 nm (ε = 7.2 cm<sup>-1</sup>M<sup>-1</sup>), pH = 9): λ<sub>max</sub> = 522 nm (ε = 6.2 cm<sup>-1</sup>M<sup>-1</sup>).

Analysis of **7**:

**IR** (KBr): 1626 cm<sup>-1</sup> ν C=O<sub>ligand</sub>.

### 2.5 Synthesis of the Ni (II) complexes of **2**

The ligand **2\*1.5HCl** (50 mg, 0.145 mmol) was added to a solution of 36.2 mg of nickel acetate \* 4H<sub>2</sub>O (0.145 mmol) in 10 ml of dry ethanol. The solution was refluxed for 2 h. The mixture was filtrated to obtain 27.1 mg (45%) of a green precipitate [Ni(H<sub>2</sub>FMedione)Cl<sub>2</sub>] (**8**). The filtrate was evaporated under vacuum to obtain 15 mg (22%) of a light blue residue [Ni(H<sub>2</sub>FMedione)(OAc)<sub>2</sub>] (**9**).

Analysis of **8**:

**MS (FAB, solvent = ethylene glycol; matrix = pNBA)**: m/z (%) = 346 (100) [M-H-2 Cl]<sup>+</sup>, 382 (65.8) [M - Cl]<sup>+</sup>.

**IR** (KBr): 1703 cm<sup>-1</sup> ν C=O<sub>ligand</sub>.

Analysis of **9**:

**IR** (KBr):  $1696\text{ cm}^{-1}$   $\nu$  C=O<sub>ligand</sub>,  $1551\text{ cm}^{-1}$   $\nu$  C=O<sub>acetate</sub>.

### 3. Results and discussion

#### 3.1. The reactions of **3** with either $\text{Co}(\text{acac})_3$ or $\text{Co}(\text{OAc})_2$

We have reacted the **H<sub>2</sub>F<sub>2</sub>dione (3)** ligand with either  $\text{Co}(\text{acac})_3$  or  $\text{Co}(\text{OAc})_2$  (Fig. 4).

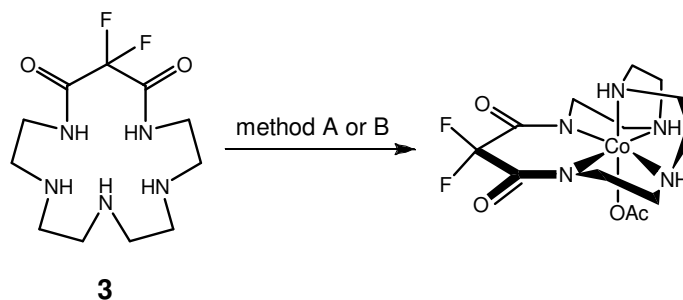
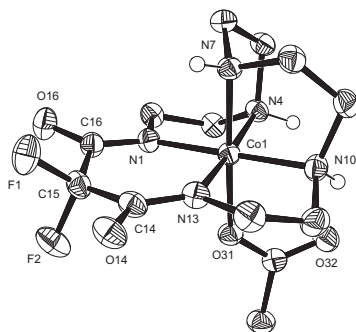


Fig. 4. Reaction of **H<sub>2</sub>F<sub>2</sub>dione (3)** by either method A or B to yield  $[\text{Co}(\text{F}_2\text{dione})(\text{OAc})]$ . Method A: i)  $\text{Co}(\text{acac})_3$ ,  $\text{CH}_3\text{CN}$ , reflux; ii)  $\text{CH}_2\text{Cl}_2$ , air; iii)  $\text{MeOH}$ ,  $\text{NH}_4\text{OAc}$ . Method B: iv)  $\text{Co}(\text{OAc})_2$ ,  $\text{EtOH}$ ; v) air.

By the first method starting with  $\text{Co}(\text{acac})_3$ , we obtained a main product, which showed a carbonyl stretching band at  $1631\text{ cm}^{-1}$ . Since the analogous IR absorption of the free ligand **3** is at  $1695\text{ cm}^{-1}$ , the shift is an indication that the three secondary amine nitrogen atoms of the ligand were coordinated to the cobalt ion as well as the two deprotonated amide nitrogen atoms. The X-ray structure of the purple crystal of  $[\text{Co}(\text{F}_2\text{dione})(\text{OAc})]\cdot\text{H}_2\text{O}$ , obtained by vapour diffusion of tetrahydropyran into a solution of methanol and ammonium acetate, further confirmed the information obtained from the IR analysis. The Co (III) centre is coordinated to the five nitrogen atoms of the ligand in an octahedral conformation, the sixth site being occupied by an acetate group (Fig. 5). The coordination environment of the metal is similar to other X-ray structures of cobalt(III) complexes with deprotonated amide groups reported in the literature [29-32].



*Fig. 5. ORTEP plot of the Co complex  $[\text{Co}(\text{F}_2\text{dione})(\text{OAc})]\cdot\text{H}_2\text{O}$ , solvent molecule and non acidic hydrogen atoms are omitted for clarity. Ellipsoids drawn with 50% probability.*

We were also able to prepare the same complex,  $[\text{Co}(\text{F}_2\text{dione})(\text{OAc})]$  (**5**), in almost quantitative yield by reacting **3** with Co(II) acetate and oxidising it subsequently with air (Fig. 4). This is in contrast to the report of Chavez et al. who had to oxidize their cobalt(II) salts with the help of hydrogen peroxide when reacting them with an acyclic diamide. In addition, when they used cobalt(II) acetate as a starting compound they observed almost no product formation [33]. Recrystallization of **5** from water and methanol yielded single crystals. The determined cell is very similar and the space group is the same compared with the above described structure of  $[\text{Co}(\text{F}_2\text{dione})(\text{OAc})]\cdot\text{H}_2\text{O}$ . Both structures are essentially isostructural, in the latter one however, a methanol molecule instead of a water solvent was found (See supporting information).

### 3.2. The reaction of **3** with $\text{Ni}(\text{OAc})_2$

A general scheme of the reaction between ligands **2** and **3** with nickel(II) is shown in Figure 6.

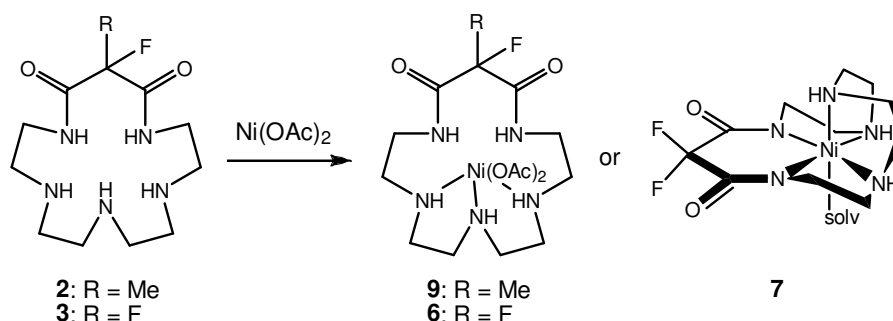


Fig. 6. Reaction of either of *H<sub>2</sub>FMedione* or *H<sub>2</sub>F<sub>2</sub>dione* with nickel(II) acetate to yield the corresponding nickel complexes **6**, **7**, and **9**.

When ligand **3** was used, the formation of the nickel complex was straight forward and the metal centre showed a different coordination mode depending on the kind of solvent mixture used during the crystallization process. Light blue crystals (**6**) were obtained from slow evaporation of an acetonitrile/tetrahydropyran mixture and were characterized by an UV-Vis absorption at  $\lambda_{\text{max}} = 528 \text{ nm}$  (buffer pH = 7,  $\epsilon = 7.2 \text{ M}^{-1} \text{cm}^{-1}$ ), and an amide carbonyl IR absorption at  $1720 \text{ cm}^{-1}$ . A single crystal analysis revealed the geometry of the complex: The nickel(II) centre is in a distorted octahedral conformation coordinated to three amine nitrogen atoms in a *mer* fashion. The other three coordination sites are occupied by the two acetate anions. One of the acetate molecules is bidentate to the nickel, while the other one is contributing as a monodentate ligand. There are four complexes in the asymmetric unit. Three of them are nearly identical and related by non crystallographic translations. In the fourth structure, the two carbonyl groups point to opposite directions (Fig. 7, right) and one of the amide hydrogen atoms forms a hydrogen bridge with a different oxygen than the other amide proton. A refinement with a cell having only one molecule in the

asymmetric unit with a disordered carbonyl group led to unsatisfactory results. In the first structure (Fig. 7, left), the dihedral angle defined by the atoms C(11)-C(1)-C(2)-O(1) is  $89.2(4)^\circ$ , and the one defined by C(2)-C(1)-C(11)-O(11) is of  $-93.6(4)^\circ$ . These values are very close to  $90^\circ$ , while in the second structure (Fig. 7, right) the angles defined by C(62)-C(61)-C(71)-O(71) and C(71)-C(61)-C(62)-O(61) are  $-117.7(3)^\circ$  and  $-161.5(3)^\circ$  respectively.

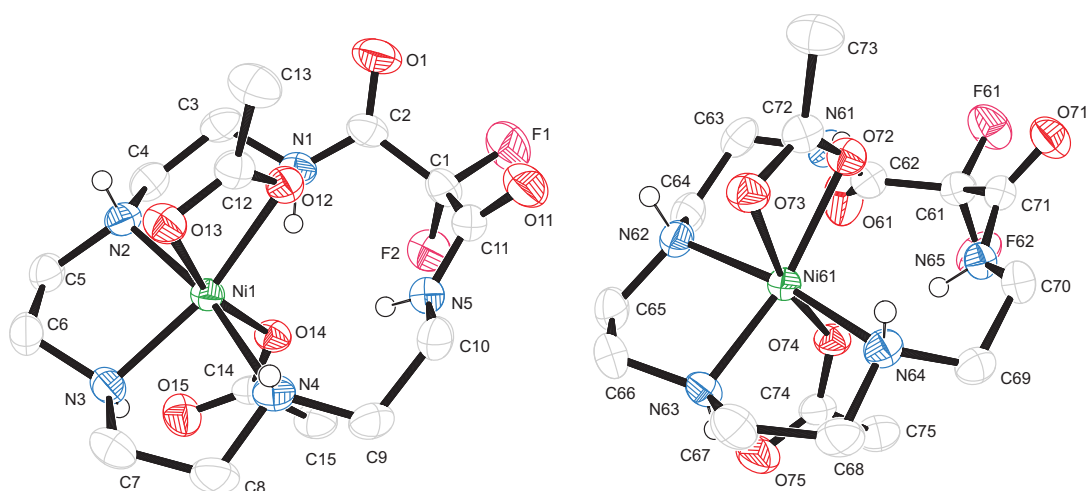


Figure 7. ORTEP plot of light blue complex  $[\text{Ni}(\text{H}_2\text{F}_2\text{dione})(\text{OAc})_2]$  (**6**). Only two different complexes out of four are shown. (Ellipsoids drawn at 50% probability; non acidic hydrogen atoms are omitted for clarity). In the left structure the carbonyl group (C2–O1) is pointing to a different orientation than in the right structure (C62–O61).

From the same nickel complex, a pink crystal (**7**) was obtained by layering diethyl ether over a methanol solution. The X-ray structure shows that the nickel(II) centre exhibits an almost perfect octahedral coordination geometry. Besides the three amine nitrogen atoms and the two deprotonated amide nitrogen atoms, the sixth coordination site is occupied by a methanol molecule (Fig. 8). The complex shows an amide carbonyl IR band at  $1626\text{ cm}^{-1}$ . Since, as above mentioned, the amide bond of the free

ligand shows an IR adsorption at  $1695\text{ cm}^{-1}$ , the shift indicates that the metal ion, once again, is coordinated to the five nitrogen atoms of the ligand.

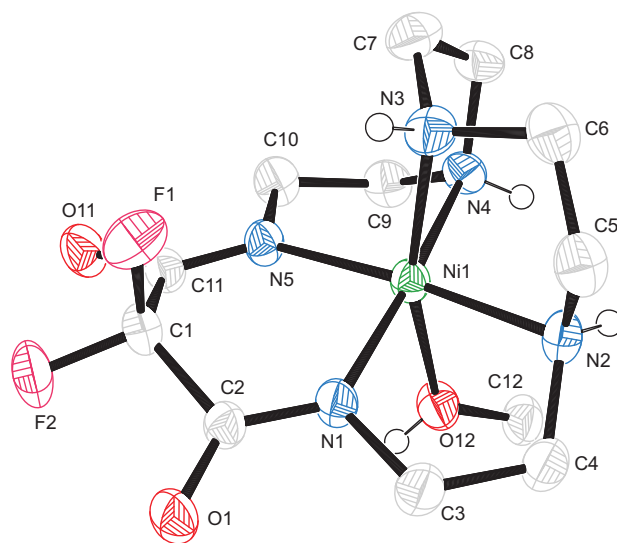


Fig. 8. ORTEP plot of the pink complex  $[\text{Ni}(\text{F}_2\text{dione})(\text{MeOH})]\cdot\text{MeOH}$  (7). (Ellipsoids drawn at 50% probability; non acidic hydrogen atoms and non-coordinating solvent molecule are omitted for clarity).

### 3.3. The reaction of 2 with $\text{Ni}(\text{OAc})_2$

The 15-fluoro-15-methyl ligand **2**, synthesised as an hydrochloride salt, was complexed with  $\text{Ni}(\text{II})$  acetate in refluxing ethanol to obtain a green precipitate and a light blue solution that, upon evaporation, gave a blue residue. The green complex shows an amide bond IR adsorption at  $1703\text{ cm}^{-1}$  while the blue one at  $1696\text{ cm}^{-1}$  indicating that, in both cases, the metal ion is not coordinated to the amide nitrogen atoms of the ligand. A green crystal of was obtained from an aqueous solution of the green powder by slow evaporation of water. The X-ray structure shows that the  $\text{Ni}(\text{II})$  centre is coordinated in an distorted bipyramidal conformation to the three secondary amine nitrogen atoms and to two chloride atoms  $[\text{Ni}(\text{H}_2\text{FMedione})\text{Cl}_2]$  (**8**) (Fig. 9).



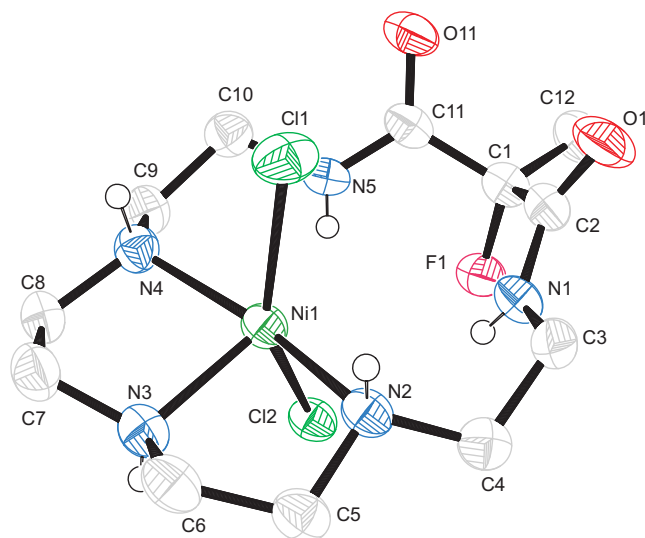


Fig. 9. ORTEP plot of complex  $[\text{Ni}(\text{H}_2\text{FMedione})\text{Cl}_2]$  (**8**) (Ellipsoids drawn at 50% probability; non acidic hydrogen atoms are omitted for clarity).

Light blue crystals of were obtained by layering diethyl ether over a methanol solution of the blue complex  $[\text{Ni}(\text{H}_2\text{FMedione})(\text{OAc})_2]$  (**9**). The X-ray structure shows that the Ni(II) centre is coordinated in a distorted octahedral mode to the three amine nitrogen atoms of the ligand and one of the acetate molecules is contributing as a mono-dentate ligand and the other as a bidentate one (Fig. 10). The N(3)- O(15) distance of 2.841 Å indicates the presence of a hydrogen bond between these two atoms.

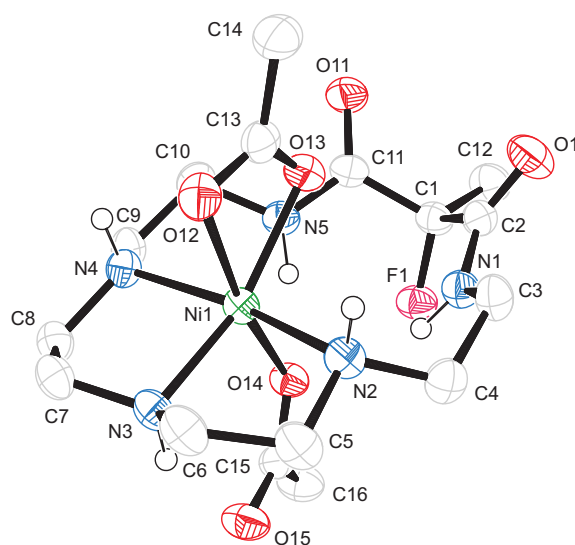


Fig. 10. ORTEP plot of complex  $[\text{Ni}(\text{H}_2\text{FMedione})(\text{OAc})_2]$  (**9**). (Ellipsoids drawn at 50% probability; non acidic hydrogen atoms are omitted for clarity).

Both X-ray structures of nickel with the **H<sub>2</sub>FMedione** (**2**) ligand show that the more electron withdrawing fluorine prefers to be in the axial position, as already seen previously for the corresponding copper and zinc complexes [5]. In all 4 cases of the N3 coordination, we have never observed that an amide oxygen coordinates to the nickel, as there is also only one case in the literature that reports such a geometry [25].

### 3.4. Cyclic voltammetry

Cyclic voltammetry was used to determine the redox potential of the Ni(II/III) couples for the nickel complexes with **2** and **3**.

Fig. 11 shows the reversible voltammograms of the two Ni complexes recorded in 0.5M Na<sub>2</sub>SO<sub>4</sub>, pH = 6 (no buffer present), at room temperature, using a glassy carbon working electrode and an Ag/AgCl reference electrode at a scan rate of 0.1 V/s.

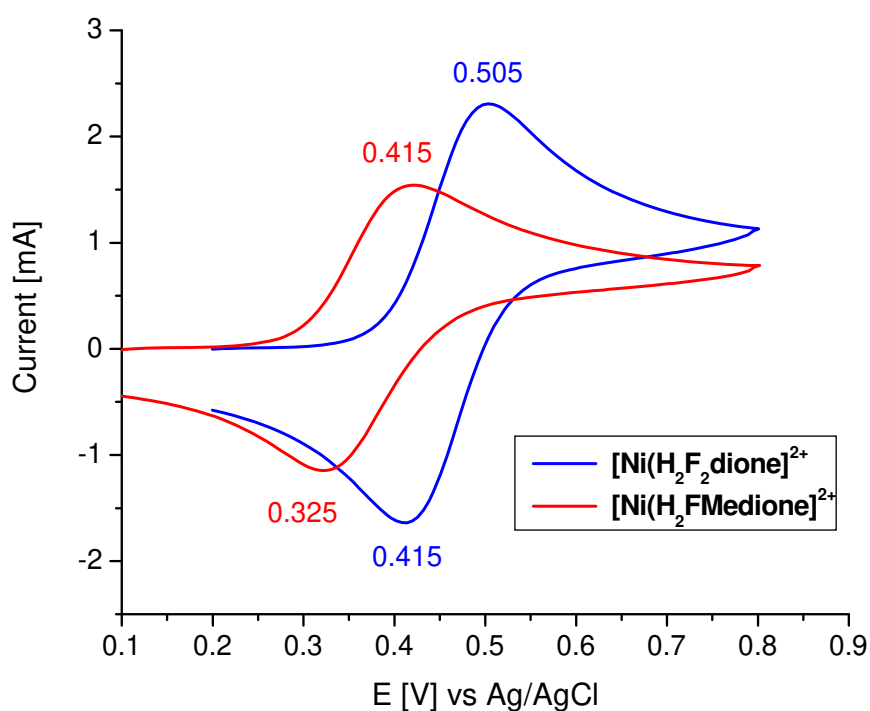


Fig. 11. Cyclic voltammograms of the nickel complexes of **H<sub>2</sub>F<sub>2</sub>dione** and **H<sub>2</sub>FMedione**. In both cases the Ni(II/III) redox couple was recorded in 0.5M Na<sub>2</sub>SO<sub>4</sub>, at pH = 6 (no buffer present), and at r.t. WE = glassy carbon; RE = Ag/AgCl.

The redox potential E° values are depending on the C-15 substitution as it is shown in Table 2. As expected, the nickel metal centre is more easily oxidized when it is coordinated by ligand **2** than by **3**, due to the electron withdrawing influence of the additional fluorine. These observations are consistent with literature reports of related systems [8,34]. It is interesting to note, that the redox potentials of Ni complexed by **2** at pH 6 and 9.2 [25] are almost the same. This would imply that at both pH values an N5 coordination is present which is again in line with the UV measurements at neutral and basic pH.

Table 2. E° redox potential of the Ni(II/III) redox couple of different Ni dione complexes<sup>a</sup>

Complex	E° Ni(II/III) [V]	Reference
<b>Ni + F<sub>2</sub>dione</b>	0.460 <sup>b</sup>	This work
<b>Ni + F<sub>2</sub>dione</b>	0.465 <sup>c</sup>	[25]
<b>Ni + FMedione</b>	0.370 <sup>b</sup>	This work
<b>Ni + Fdione</b>	0.355 <sup>c</sup>	[9]
<b>Ni + dione</b>	0.285 <sup>d</sup>	[8]
<b>Ni + Me<sub>2</sub>dione</b>	0.215 <sup>d</sup>	[35]

<sup>a</sup> values versus Ag/AgCl.

<sup>b</sup> In 0.5M Na<sub>2</sub>SO<sub>4</sub>, at pH = 6 (no buffer present), at r.t., scan rate = 0.1 V/s.

<sup>c</sup> In 1.0M K<sub>2</sub>HPO<sub>4</sub> buffer pH = 9.2, at r.t.

<sup>d</sup> In 0.5M Na<sub>2</sub>SO<sub>4</sub>, at pH = 9.5, scan rate = 2 mV/s.

Complexes **Ni(Fdione)** and **Ni(dione)** are not air stable and react in solution with O<sub>2</sub>. Complexes **[Ni(H<sub>2</sub>FMedione)(OAc)<sub>2</sub>]** and **[Ni(H<sub>2</sub>F<sub>2</sub>dione)(OAc)<sub>2</sub>]**, on the other hand, do not show this reactivity towards O<sub>2</sub>. A possible explanation for this different behaviour is given by Cheng *et al.* [34] who showed that the O<sub>2</sub> reaction is not dependent on the redox potential of the coordinated nickel, but on the presence of a hydrogen substituent, or on the ability to oxidise the C-15.

#### 4. Conclusions

In this publication we have presented the synthesis of the novel **[Co(F<sub>2</sub>dione)(OAc)]** complex from different cobalt sources. We showed that the formation of the cobalt(II) complex which is then oxidized to the oxidation state (III) is the far superior route compared to the option of using cobalt(III) as the starting material. Furthermore we have studied in detail the reaction of either **H<sub>2</sub>FMedione (2)** or **H<sub>2</sub>F<sub>2</sub>dione (3)** with nickel(II) to give the corresponding complexes. Depending upon the solvent, N3 or, after a double deprotonation, N5 coordination could be observed and characterized in the solid state. 6 complexes of both metals could be crystallized and analysed by single crystal analysis. Cyclic voltammetry revealed that the Ni(II/III) redox potentials are becoming more positive with the increasing number of fluorine atoms due to the electron withdrawing property of fluorine itself which is reducing the electron richness of the metal ion.

Supporting information:

ORTEP plot and crystallographic data of the Co complex **[Co(F<sub>2</sub>dione)(OAc)]** \*MeOH.

#### Acknowledgements

This work was supported by the Swiss National Science Foundation and the Forschungskredit of the University of Zürich. We thank Prof. R. Alberto and his whole group as well as Dr. S. Gupta for valuable discussions. We further thank B.

Spichtig for performing the FAB MS analysis, B. and H. Spring for doing the elemental analysis.

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